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MECHANICAL WORKING IN THE PRESENCE OF A MULTI-PURPOSE COOLING LUBRICANT

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The present invention relates to a multi-purpose aqueous cooling lubricant suitable for the mechanical working of many different metals and alloys. The cooling lubricant containing as essential components a phosphate ester compound and a dicarboxylic acid contributes to excellent corrosion inhibiting and lubrication properties.

The mechanical working of metals is often performed in the presence of an aqueous cooling lubricant. A disadvantage of many aqueous cooling lubricants is that they frequently contain an iron corrosion inhibitor, such as monoethanolamine, diethanolamine or triethanolamine, which has a detrimental effect and causes discoloration and dissolution when used with cobalt, copper, aluminum, lead or zinc or alloys thereof. Besides the corrosion, any dissolved metal may also constitute a human health and environmental hazard and is difficult to remove from water in the process of disposal of the cooling lubricant.

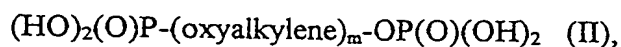
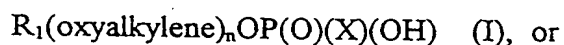
In order to mitigate the negative effects of alkanol amine, anionic surface active components with long aliphatic groups, such as groups with 14-44 carbon atoms have been added. Exemplary components are phosphate esters, fatty acids and dimer acids. Their protective action depends on the formation of water-insoluble, organic layers on the metal surfaces. If, however, dissolved di- or trivalent metals exist in the cooling lubricant, the anionic components will form water-insoluble salts with these metals ions. This may sometimes further increase the corrosion inhibiting effect, but it will also lead to the formation of undesirable a sticky precipitation, which e.g. tends to interfere with the purification of the cooling lubricant. Another drawback is the difficulty to remove the hydrophobic layers formed on the metal surfaces. If they are not removed, they could cause problems in the subsequent surface treatments, for example pickling, phosphatizing, galvanizing or other metal depositing processes. The presence of the long chain anionic components may also cause undesirable foaming and scum.

US patent 4 315 889 discloses a method of reducing the release of cobalt by performing the metal working in the presence of a cooling lubricant containing, as an active component, a specific triazole or thiadiazole compound. However, since these active compounds are consumed in the presence of ethanolamines, the aqueous cooling lubricant has to be regularly upgraded.

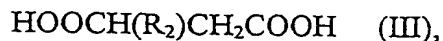
EP-A-0180561 describes the use of a tertiary alkanol amine compound for reducing the release of cobalt. According to the application the tertiary alkanol amine compound can advantageously be combined with carboxylic acids to further increase the protection against the release of cobalt and the corrosion of iron.

DE-OS-2 943 963 discloses the use of an alkanolamine salt of alkenyl succinic acid as corrosion inhibitor in aqueous solutions and US patent 4 670 168 describes a metalworking composition containing a water-soluble polyalkyleneglycol and a neutralised or partly neutralised alkenyl succinic acid.

According to the present invention it has now been found that the above mentioned problems may be reduced or eliminated by using a combination of a phosphate ester and a dicarboxylic acid as a lubricant and anti-corrosion agent in an aqueous metal working liquid, whereby the dissolution and discoloration of several metals, such as cobalt, copper, zinc, lead, aluminum and iron, and their alloys are effectively hampered. In more detail, the present invention relates to a process for the mechanical working of metals, which is performed in the presence of an aqueous cooling lubricant having a pH of 6-10 and containing a phosphate ester of the formula



where R_1 is an alkyl group with 1-12 carbon atoms, oxyalkylene is a group containing 2-4 carbon atoms, n is a number from 1-20, preferably 4-15, X is hydroxyl, the group $R_1\text{O}$ or the group $R_1(\text{oxyalkylene})_n\text{O}$, where R_1 , n and oxyalkylene have the above mentioned meanings, and m is a number from 4-40, preferably 5-20 or a salt thereof, and an alkenyl substituted succinic acid of the formula



where R_2 is an aliphatic group with 4-10 carbon atoms, or a salt thereof, or a mixture of the compounds I, II and III. The total amount of compounds I and II is from 0,2 to 5% by weight, preferably 0,4-3% by weight and the amount of compound III is from 0,2 to 5% by weight, preferably 0,4-3% by weight. The salts of the phosphate ester and the succinic acid are preferably formed of monovalent cations, such as potassium and sodium.

In the phosphate esters of formulae I and II, the $(\text{oxyalkylene})_n$ group and $(\text{oxyalkylene})_m$ group respectively, are suitably selected in such a way that the esters will be water-soluble or easily dispersible in water. Preferably the $(\text{oxyalkylene})_n$ group contains at least partially oxypropylene units and most preferably only oxypropylene units. The

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aliphatic group R_1 can be saturated or unsaturated, straight or branched and contains preferably 2-8 carbon atoms. The group X is preferably a hydroxyl or the group $R_1(\text{oxyalkylene})_n\text{O}$. Preferably the phosphate ester of formula I consists of at least 50% by weight of monoesters. In formula II the polyoxyalkylene chain preferably consists at least partially of oxyalkylene groups with 3-4 carbons atoms and m preferably is at least 6, since these diphosphate esters beside the corrosion inhibiting effect give a considerable contribution to the lubrication. Especially suitable are those diphosphate esters, which contain a polyoxypropylene chain with 8-15 oxypropylene units.

The succinic acid of formula III contains an aliphatic group R_2 which can be a straight or branched alkenyl. Examples of alkenyl groups are octenyl, decenyl, di(isobutenyl) and tri(propenyl). Preferably the alkenyl group contains 7-9 carbon atoms. The succinic acids of formula III exhibit in addition to their excellent lubrication and anti-corrosion also low foaming, which is of essential importance in a metal working cooling lubricant.

The cooling lubricant can also contain a number of other additives, such as additional corrosion-inhibiting additives and lubricants, pH-regulating or controlling additives, bactericidal agents, viscosity-increasing additives, solubilizers, perfumes, colourants etc.

Examples of suitable additional corrosion inhibitors are amine compounds, such as triazole and thiadiazole compounds and inorganic compounds, such as alkali metal hydroxides and boric acid, and reaction products between boric acid and/or carboxylic acids and organic reactants, such as alkanol amines. The content of these additional corrosion inhibitors may be up to 3% by weight of the cooling lubricant.

Although the cooling lubricant containing the anionic surfactants I, II and III has an adequate lubrication ability for most applications it may be occasions where improved lubrication is desired. Examples of suitable lubricants to be incorporated into a cooling lubricant according to the invention are those selected from the group consisting of esters or amides of mono- or dicarboxylic acids having at least 12 carbon atoms in the acyl groups, organic aliphatic phosphate esters containing one or two aliphatic groups with 6-18 carbon atoms, nonionic alkylene oxide adducts with a molecular weight above 400, such as polypropylene glycols, glycols of randomly distributed propyleneoxy and ethyleneoxy groups and block polymers of propylene oxide and ethylene oxide, and mixtures thereof.

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The content of these additional lubricants may be up to 3% by weight of the cooling lubricant ready for use.

The solubilizers are usually low molecular weight compounds containing at least one hydroxyl. The molecular weight is normally below 400. Examples of suitable solubilizers are propyleneglycol, methyl dipropyleneglykol, ethyl diethyleneglycol, butyl diethyleneglycol and butyl triethyleneglycol.

When preparing a cooling lubricant according to the invention, it is suitable to first prepare a concentrate, for example by first mixing the anionic compounds I, II and III and water, and then the supplementary ingredients. The amount of water is suitably between 5 and 80% by weight of the concentrate. A typical concentrate according to the invention has the following composition:

anionic compounds I, II and III	20-95, preferably 50-90% by weight
additional corrosion inhibitors	0-30, preferably 0-15% by weight
additional lubricants	0-30, preferably 0-15% by weight
water	5-80, preferably 10-50% by weight
other ingredients	0-30, preferably 0-15% by weight,

the weight ratio between the compounds I and/or II and compound III being from 1:15 to 15:1, preferably from 1:5 to 5:1.

The total amount of the additional corrosion inhibitors, the additional lubricants and the other ingredients is often 5-40% by weight of the concentrate. Before the concentrate is used, it is diluted with water so that the cooling lubricant ready for use will have a total content of the anionic compounds I, II and III of 0.5-10% by weight, preferably 2-6% by weight.

The present invention is further illustrated by the following Example.

Example

Three water-based lubricants A, B and C were prepared by adding 20 grams of octenyl succinic acid, 20 grams of *n*-butyl-(C₃H₆O)₁₀OPO₃H₂, or 10 grams of octenyl succinic acid and 10 grams of *n*-butyl-(C₃H₆O)₁₀OPO₃H₂, respectively, to 980 grams of water of a water hardness of 17°dH. The pH value of the cooling lubricants were adjusted to 9 by addition of KOH. The lubrication and corrosion-inhibiting ability of the cooling lubricants were tested. The lubrication was determined by measuring the wear scar obtained in modified Timken machine using steel rings A4138 with an outer diameter of 35

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mm. The tests were performed during 2 and 5 minutes at a temperature of 45°C. The corrosion of Fe, Al, Co, Cu and brass was determined by the following test methods.

Fe-corrosion tests were done by placing 30 grams of cast iron chips evenly spread on a circular filter paper with a diameter of 90 mm. 1.25 gram of one of the cooling lubricants was dispensed at the centre of the filter paper, which was placed in a plastic Petri dish and covered by a lid. The corrosion taken place after 24 hours was determined by visually inspection of the rust staining according to a scale, where 0= no corrosion, 1= one stain, 2= two or three stains, 3= more than three stains up to 10% of the paper surface discoloured, 4= between 10 and 25% of the paper surface discoloured, and 5= more than 25% of the paper surface discoloured.

Co and Cu corrosion tests were performed by assessing the amount of leached cobalt and copper obtained, when a 20 ml glass vial containing 5 glass beads, 5 mg of fine powder of cobalt or copper and 10 ml of one of the fluids was shaken for 7 days. The amount of cobalt or copper dissolved was measured by use of an atomic absorption spectrophotometer (AAS). Initial screening of the fluids was done by using analytical sticks from Merck and only samples, which were found to contain less than 30 ppm of cobalt or copper were subjected to AAS analysis.

Since brass and aluminium are often used in applications where visual appearance is important an immersion test was performed to show the degree of discoloration caused by the test solutions. Strips of 5 mm width and 60 mm length of each metal were placed in separate glass vials and tests solutions were added in an amount sufficient to cover half the length of the upright standing strips. The corrosion was visually determined after 7 days. The discoloration of the strips was measured according to a scale from 0 to 5, where 0 represent no corrosion, 1 indicate that up to 5% of the surface is black, 2 that 5-10% of the surface is black, 3 that 10-25% of the surface is black, 4 that 25-90% of the surface is black, and 5 that 90-100% of the surface is black.

The following results were obtained.

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Table Corrosion and Timken Tests

Formulation Symbol	Corrosion					Timken, mm	
	Fe	Al	Brass	Co	Cu	2 min	5 min
A	0	0	0	0	5	0.97	1.07
B	4	0	1	0	10	0.83	1.17
C	0	0	0	0	5	0.83	1.03

From the results it is evident that the cooling lubricant C of the invention has excellent anti-corrosion properties and is superior to the comparison compositions as regards the lubrication ability.

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